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(54) Title: PROCESS FOR THE HYDROGENATION OF A POLYMER COMPOSED OF DIENE MONOMER UNITS AND A NITRILE GROUP-CONTAINING MONOMER UNITS

(57) Abstract: Process for the hydrogenation of a polymer composed of conjugated diene monomer units and a nitrile group-containing monomer units, in which hydrogenation is carried out in the presence of hydrazine, and an oxidizing compound, with the hydrogenation being carried out in the presence of an antioxidant. It is preferred for NBR to be used as polymer.



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5 PROCESS FOR THE HYDROGENATION OF A POLYMER COMPOSED OF
 DIENE MONOMEER UNITS AND A NITRILE GROUP-CONTAINING
 MONOMER UNITS

 The invention relates to a process for the
hydrogenation of a polymer composed of conjugated diene
10 monomer units and nitrile group-containing monomer
units, in which hydrogenation is carried out in the
presence of hydrazine and an oxidizing compound.

 It is possible to wholly or partially
hydrogenate the double bonds present in the polymer
15 chain of polymers that are composed of conjugated diene
monomer units and nitrile group-containing monomer
units, such as for instance nitrile butadiene rubber
(NBR). After hydrogenation, the polymers are, for
instance, less susceptible to oxidative degradation at
20 elevated temperature and the polymers can be applied,
for instance, under the bonnet in cars or even in the
engine block.

 Current commercial processes for
hydrogenating such polymers are very cumbersome and
25 costly. NBR is for instance dissolved in a suitable
solvent and then hydrogenated with hydrogen at a high
pressure and a high temperature in the presence of a
noble metal catalyst. The catalyst and the solvent must
subsequently be removed in a separate process step.

30 In addition, when high degrees of
hydrogenation are achieved, side reactions take place
that result in undesired branching of the polymer and
even give rise to gelation.

 US-4,452,950 discloses the hydrogenation of
35 NBR in the form of an aqueous dispersion in the
presence of hydrazine, an oxidizing compound and a
metal compound as catalyst. Following polymerization,

NBR in itself is usually already present as an aqueous dispersion in the form of a latex. The polymer may also be formed as an aqueous dispersion. A metal compound of for example copper or iron is used as catalyst.

5 This in itself yields a simplified process for the hydrogenation, but a high degree of hydrogenation is difficult to achieve.

 It is the aim of the invention to provide a process that does not have the above-mentioned drawback
10 or has that drawback only to a much lesser extent.

 Surprisingly, this aim is achieved by the hydrogenation being carried out in the presence of an antioxidant comprising more than 6 carbon atoms and chosen from a derivative of a substituted aromatic
15 alcohol, of dihydroquinoline, of benzimidazole or of an aromatic secondary amine.

 In the process of the invention, a higher degree of hydrogenation is attained under otherwise equal conditions. A further advantage of the process of
20 the invention is that, in comparison with the known process, side reactions are at least strongly suppressed or even absent. Consequently, the development of undesired branching of the polymer or even the development of undesired gelation is avoided,
25 so that the polymer can readily be compounded and can readily be processed to form moulded parts.

 US-A-5221714 discloses the teaching of Zhong and Lim whereby o-phenylenediamine can be utilized to catalyse the reaction of oxygen with
30 residual hydrazine in an aqueous emulsion of rubber. However the above teaching learns the use of compounds with less than 6 carbon atoms which form complexes with the catalyst and further catalyse the hydrogenation reaction. These compounds have no effect on the

formation of crosslinks.

While US-5,424,356 discloses hydrogenation of NBR which is polymerized in the presence of a polymerizable antidegradant, it does not appear from
5 that patent that the use of such NBR may have a favourable effect on how the hydrogenation reaction proceeds. The use of NBR that is polymerized in the presence of an antidegradant is excluded in the process of the invention.

10 Crosslinking of the latex during the hydrogenation process as described in United States Patent US 4,452,950 is mentioned in US 5,039,737 and US 5,442,009. Both patents disclose a process for breaking up the gel structures through post-treatment with
15 ozone.

The unsaturated polymers that can be hydrogenated via the process of the present invention contain for example 5-95% by weight of the conjugated diene-monomer unit and 95-5% by weight of the nitrile group-containing monomer unit. Preferably, the polymer
20 contains 50-80 % by weight of the conjugated diene-monomer unit and 20-50 % by weight of the nitrile group-containing monomer unit. More preferably, the polymer contains 60-70 % by weight of the conjugated
25 diene-monomer unit and 30-40 % by weight of the nitrile group-containing monomer unit. Specific examples of conjugated diene-monomer units are 1,3-butadiene, 2,3-dimethyl butadiene, isoprene and 1,3-pentadiene. It is preferred for 1,3-butadiene to be used. Specific
30 examples of a nitrile group-containing monomer units are acrylonitrile and methacrylonitrile. It is preferred for acrylonitrile to be used.

It is preferred for NBR to be used as polymer.

The polymers used in the process of the invention can be prepared by various processes such as emulsion polymerization, solution polymerization or bulk polymerization. Preferably, the polymers are prepared by emulsion polymerization, because in that case the polymer becomes available as a latex right away.

During hydrogenation, the polymers preferably are present in the latex form. The latex form is an aqueous emulsion of polymer, in which sundry additives such as soap and stabilisers may be present. A description of the latex form which is suitable for, for example, the hydrogenation of unsaturated polymers via the process of the invention is given in US 5,442,009.

The polymer content of the latex is in the range from for example 1 to 70 % by weight, preferably between 5 and 40 % by weight.

It is possible for hydrazine to be present during the process of the invention in as much as it is added as such. It is also possible for a hydrazine-releasing compound to be added, such as hydrazine hydrates, hydrazine acetate, hydrazine sulphate and hydrazine hydrochloride. If the unsaturated polymer is hydrogenated in latex, use is preferably made of hydrazine and hydrazine hydrate.

Hydrazine preferably is present in a molar ratio of from 0.1:1 to 100:1 relative to the double bonds in the polymer chain. Preferably, this ratio lies between 0.8:1 and 5:1, most preferably between 0.9:1 and 2:1.

Examples of oxidizing agents that are suitable for use in the process of the invention are air, oxygen, ozone, peroxides, hydroperoxides, iodine,

iodates, hypochlorite and similar compounds. Particularly suitable oxidizing agents are chosen from the group comprising peroxides and hydroperoxides. Most preferably, use is made of hydrogen peroxide.

5 The oxidizing compound is present in the polymer chain at a molar ratio of between 0.1:1 and 100:1 relative to the double bonds. This ratio preferably is between 0.8:1 and 5:1, most preferably between 0.9:1 and 2:1.

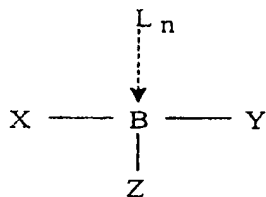
10 Examples of suitable antioxidants are given in Rubber Technology Handbook (ISBN 1-56990-145-7 (US), (Hanser/Gerdner Publications Inc., Cincinnati Ohio 1996), page 269. Specific examples of derivatives of a substituted aromatic alcohol, of dihydroquinoline, of
15 benzimidazole or of an aromatic secondary amine, comprising more than 6 carbon atoms are derivatives of p-phenylenediamine, of trimethyl-dihydroquinoline, of naphthylamine and of mercaptobenzimidazole. It is preferred for a derivative of p-phenylenediamine to be
20 used. Most preferably, N-isopropyl-N'-phenyl-p-phenylenediamine is used.

 As antioxidant use is preferably made of a compound that is insoluble in water. Preferably, the antioxidant is added to the polymer prior to
25 hydrogenation. It is preferred for the antioxidant to be added to the aqueous dispersion of the polymer in the form of an emulsion.

 Good results are achieved when the antioxidant is added in an amount of 0.1-1.0 % by
30 weight relative to the amount of polymer. Preferably, the antioxidant is added in an amount of 0.1-0.5 % by weight relative to the amount of polymer. The hydrogenation preferably is carried out in the presence of a catalyst. Suitable catalysts are

compounds which contain an element from group 13 of the Periodic Table of the Elements as published on the inside of the cover of the Handbook of Chemistry and Physics, 67th edition, 1986-1987 in accordance with the
5 latest IUPAC nomenclature.

It is preferred for the catalyst to contain boron (B). Examples of suitable B-containing catalysts are compounds of the general formula



10

where X, Y and Z are chosen independently of one another from the group comprising R, OR, OOR, NR₂, SR, PR₂, OC(=O)R and halogen atoms, where R is a H atom or
15 an alkyl, aryl or cycloalkyl group having 1-20 carbon atoms, or a hydrocarbon group having 1-20 C atoms and containing a heteroatom from groups 14, 15, 16 and 17 of the Periodic Table of the Elements;

L is an electron-donating ligand, such as water, an
20 amine, pyridine, bipyridine, triazine, a pyrrole compound, an imidazole compound, a pyrazole compound, a pyrimidine compound and a pyrazine compound, an ester, ether, a furan, tetrahydrofuran, pyrans, dioxan, phosphine, phosphide, phosphate or a thio compound and
25 n = 0 or 1.

More preferably, a borate or a peroxyborate is used. Yet more preferably, boric acid (H₃BO₃) is used.

Also suitable for use as catalyst are
30 compounds that contain a metal atom with an oxidation

number of at least 4.

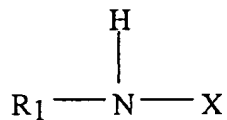
Examples of suitable compounds are compounds that contain a titanium atom with oxidation number 4 (Ti(IV)), a vanadium atom with oxidation
5 number 5 (V(V)), a molybdenum atom with oxidation number 6 (Mo(VI)) or a tungsten atom with oxidation number 6 (W(VI)). Preferably, a compound which contains the W(VI) atom is used as catalyst. More preferably, a salt of tungstic acid is used. Most preferably, a
10 sodium salt or potassium salt of tungstic acid is used.

The benefits of the present invention become especially apparent if a metal ion activator is used as catalyst for example a copper or an iron salt, like cuprous chloride or ferrous sulphate.

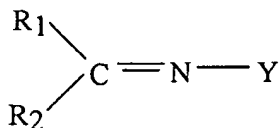
15 The molar ratio of the catalyst to the double bonds in the polymer chain is between for example 1:1000 and 10:1. The ratio preferably is between 1:50 and 1:2.

The order in which the compounds are added
20 for the hydrogenation reaction may in principle be random. Preferably, however, the oxidizing compound is added after hydrazine, more preferably in such a way that the concentration of the oxidizing compound remains low during the hydrogenation reaction.

25 Although in the process of the invention the development of branches or gel particles in the hydrogenated polymer is very strongly suppressed in comparison with the known process, a further improved process of the invention is obtained if a compound that
30 satisfies formula I is added after the hydrogenation or if a compound that satisfies formula II is added before, during or after hydrogenation.



formula I



formula II

5

where R_1 is a hydrogen atom, an alkyl or cycloalkyl group with 1-30 carbon atoms, or an aromatic group with 6-30 carbon atoms and

R_2 is an alkyl or cycloalkyl group with 1-30 carbon atoms, or an aromatic group with 6-30 carbon atoms,

X is chosen from the group comprising $-\text{R}_3$, $-\text{OR}_4$,

$-\text{SR}_4$, $-\text{NR}_5\text{R}_6$, where R_3 , R_4 and R_5 are a hydrogen atom, an alkyl or cycloalkyl group with 1-30 carbon atoms or an aromatic group with 6-30 carbon atoms and R_6 is an alkyl or cycloalkyl group with 1-30 carbon atoms or an aromatic group with 6-30 carbon atoms

Y is chosen from the group comprising $-\text{R}_7$, $-\text{OR}_8$,

$-\text{SR}_8$, $-\text{NR}_9\text{R}_{10}$ and $-\text{N}=\text{CR}_{11}\text{R}_{12}$, where R_7 , R_8 , R_9 , R_{10} , R_{11} and R_{12} are a hydrogen atom, an alkyl or cycloalkyl group with 1-30 carbon atoms or an aromatic group with 6-30 carbon atoms, and it being possible for R_3 - R_{12} to also contain one or more heteroatoms from the groups 13, 14, 15, 16 or 17 of the Periodic System of the Elements.

Periodic System of the Elements should be taken to be the Periodic System as defined above.

The addition of such a compound causes strong or complete suppression of the crosslinking reaction. Moreover, addition of the compounds according to the invention has the advantage that no ozonolysis
5 needs to be carried out in order to sever crosslinked polymer chains.

It is preferred for compounds to be used in which R_1 is a H atom.

Examples of compounds that satisfy formula
10 I are primary and secondary amines, hydroxylamine, derivatives of hydroxylamine and substituted hydrazines, dithiocarbamylsulphenamide compounds, thiuram compounds and dithiocarbamate compounds. Specific examples are methylamine, ethylenediamine,
15 dodecylamine, ethanolamine, cyclohexyldiamine, o-phenylenediamine, 3,4-toluenediamine, 1,8-naphthalenediamine, aniline, methylhydrazine, phenylhydrazine, o-aminophenol, o-aminobenzoic acid, hydroxylamine, N-isopropyl hydroxylamine, O-
20 methylhydroxylamine, O-t-butylhydroxylamine and the sulphur compounds tetramethylthiuram disulphide, N-oxydiethylene dithiocarbamyl-N'-oxydiethylene-sulphenamide. Preferably, use is made of compounds that satisfy formula I where R_3 is an aromatic group with 6-
25 15 carbon atoms, R_4 is a hydrogen atom, or an alkyl group with 1-5 carbon atoms, R_5 is a hydrogen atom, an alkyl group with 1-6 carbon atoms or an aromatic group with 6-10 carbon atoms and R_6 is an alkyl group with 1-6 carbon atoms or an aromatic group with 6-10 carbon
30 atoms, it being possible for R_3 - R_6 to also contain one or more heteroatoms from the groups 13, 14, 15, 16 or 17 of the Periodic System of the Elements. Most preferably, hydroxylamine or orthoaromatic diamines are used.

Examples of compounds that satisfy formula II are imines, azines, hydrazones, semicarbazones, oximes and benzothiazoles. Specific examples are N-phenylbutyl imine, N-isopropylbenzaldehyde imine, acetone azine, benzaldehyde azine, cyclohexanone azine, benzaldehyde hydrazone, benzophenone hydrazone, benzaldehyde oxime, p-nitrobenzaldehyde oxime, o-, p-, and m-chlorobenzaldehydeoxime, cyclohexanone oxime, acetoxime, 2-mercaptobenzothiazole, N-cyclohexyl-2-benzothiazole sulphenamide methyl ethyl ketone oxime, benzophenone oxime.

Preferably, compounds are used that satisfy formula II, where R_7 is an aromatic group that contains 6-10 carbon atoms, R_8 is a hydrogen atom or an alkyl group with 1-6 carbon atoms, R_9 - R_{11} are a hydrogen atom, an alkyl group with 1-6 carbon atoms, or an aromatic group with 6-10 carbon atoms, and R_{12} is an alkyl group with 1-6 carbon atoms or an aromatic group with 6-10 carbon atoms, it being possible for R_7 - R_{12} to also contain one or more heteroatoms from the groups 13, 14, 15, 16 or 17 of the Periodic System of the Elements. More preferably, use is made of compounds that satisfy formula II where Y is an OH-group. Most preferably, use is made of a compound that satisfies formula II where Y is an OH group, R_1 is a hydrogen atom and R_2 is an alkyl or cycloalkyl group with 1-15 carbon atoms or an aryl group with 6-10 carbon atoms. Examples of these compounds are benzaldehyde oxime, propionaldehyde oxime and dodecylaldehyde oxime.

Compounds that satisfy the description of formula I are added after the hydrogenation reaction, preferably before or during separation of the hydrogenated polymer, more preferably to the hydrogenated polymer during a post-treatment.

Surprisingly, this suppresses the crosslinking reaction in the hydrogenated polymer even further. In particular, crosslinking during storage of the polymer is suppressed more strongly. This is important for instance if a hydrogenated polymer with a high molecular weight is used. The occurrence of a crosslinking reaction has a strong effect on the rheological properties of such a polymer.

Hydroxylamine is preferably added to the hydrogenated polymer in the form of an aqueous solution. Most preferably, the hydrogenated polymer is contacted with a 1-20 wt.% solution of hydroxylamine in water.

More preferably, a combination of an oxime, of the general formula II, where Y is an OH group, R₁ is a hydrogen atom and R₂ is an alkyl or cycloalkyl group with 1-15 carbon atoms or an aryl group with 6-10 carbon atoms, and hydroxylamine is added. The oxime is then preferably added before or during the hydrogenation of the polymer, while the hydroxylamine is added during post-treatment of the hydrogenated polymer crumb.

Even more preferably, a compound according to formula I or II is present during kneading of hydrogenated polymer at elevated temperature. The kneading temperature preferably lies between 50 and 300°C, most preferably between 100 and 200°C.

Most preferably, the hydrogenated polymer is kneaded in the presence of a compound according to formula I, with also a carbonyl group-containing compound (for instance an aldehyde or ketone) being present. Most preferably, a ketone is used. Examples of suitable ketones are acetophenone, benzophenone and 2-dodecylketone. This further accelerates the degradation

of crosslinks by the action of the compounds according to the invention, so that the kneading time and/or the kneading temperature can be reduced. Special preference is given to o-aromatic diamines as the compounds according to formula I in combination with a ketone. Preferably, o-phenylenediamine or 3,4-toluenediamine are used.

The hydrogenation can be carried out batch-wise or continuously. Sealed or opened vessels may be used.

The amount of double bonds to be hydrogenated may represent only a proportion of the total amount of double bonds present in the polymer chain.

The degree of hydrogenation is $(A/B) \times 100\%$, where A is the amount of double bonds that is saturated as a result of the hydrogenation reaction and B is the initial amount of double bonds. The process of the present invention provides polymers that have a degree of hydrogenation higher than, say, 60%. Preferably, the degree of hydrogenation is higher than 80%. The process is eminently suitable for preparing polymers having a degree of hydrogenation higher than 90%.

The hydrogenation reaction temperature is between 0° and 250°C. The temperature preferably is between 20° and 150°C. A reaction temperature between 30° and 80°C is particularly preferable.

During hydrogenation in a latex, a minor amount of solvent for the unsaturated polymer may be present. In that case, the amount of solvent may vary between 0 and 20% by weight (solvent relative to polymer).

The hydrogenation time normally is between 1 minute and 24 hours. The hydrogenation time

preferably is between 1 hour and 12 hours.

The process is illustrated by the following examples without being limited thereto.

In almost all cases the degree of
5 hydrogenation was determined with the aid of ^1H -NMR in a Bruker 200 MHz instrument. The measurement was conducted on precipitated polymer that was dissolved in deuterated chloroform. The degree of hydrogenation was calculated from the ratio of the integrals of the
10 olefinic protons, which are between 5.2 and 5.6 ppm, and the proton adjacent to the nitrile group, being between 2.35 and 2.65 ppm.

Comparative Experiment A

15 A mixture of 620 grams of hydrazine monohydrate, 100 grams of boric acid, 500 grams of water and a few drops of silicone oil was added to 4 litres of latex which contained 25% by weight of NysinTM 33-3, an NBR containing 67% by weight of butadiene
20 monomer units, in a stirred vessel. After the temperature had been adjusted to 40°C, 1615 grams of a 30% m/m (= on a mass basis) solution of hydrogen peroxide in water were added in 12 hours.
Next, 50 grams of the latex were precipitated in 400
25 grams of a 0.5% (m/m) solution of $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ and in a 50% (m/m) solution of hydroxylamine in water for 48 hours. The degree of hydrogenation was 82%.

Example I

30 Comparative experiment A was repeated except that there had been added to the latex 1 % by weight of the antioxidant Flexone 11 L based on the amount of NysinTM 33-3. Flexon 11L is an emulsion of (N-1,4-dimethylphenyl(-N'-phenyl)-p-phenylenediamine
35 (7-PPD). The degree of hydrogenation appeared to be

89%.

Comparison of Example 1 and Comparative Experiment A indicates that, by adding the antioxidant in Example I, a higher degree of hydrogenation is
5 achieved under otherwise equal conditions.

Comparative Experiment B

500 grams of latex were separated from the hydrogenated latex in Comparative Experiment A. The
10 polymer was precipitated out of the latex by adding drop-wise 15 grams of a 36% (m/m) solution of $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ and with vehement stirring. Next, the precipitated polymer was dried in air at 70°C in about 16 hours. The polymer subsequently completely dissolved in
15 chloroform.

Next, a mixture of 40 grams of the polymer and 2 grams of o-phenylenediamine were kneaded in a Brabender TM plasticorder at a temperature of 150°C . After 10 minutes an attempt was made to dissolve the
20 polymer in chloroform. At that point the polymer was found to contain gel particles.

Example 2

Comparative example B was repeated except
25 that the hydrogenated latex obtained in Example 1 was used. This polymer was found to completely dissolve in chloroform even after kneading in the Brabender TM plasticorder.

CLAIMS

1. Process for the hydrogenation of a polymer
composed of conjugated diene monomer units and a
5 nitrile group-containing monomer units, in which
hydrogenation is carried out in the presence of
hydrazine, and an oxidizing compound,
characterized in that the hydrogenation is
carried out in the presence of an antioxidant
10 comprising more than 6 carbon atoms and chosen
from a derivative of a substituted aromatic
alcohol, of dihydroquinoline, of benzimidazole or
of an aromatic secondary amine with the use of
NBR that is polymerized in the presence of an
15 antidegradant being excluded.
2. Process according to Claim 1, characterized in
that NBR is used as polymer.
3. Process according to any one of the claims 1-2,
characterized in that the aromatic secondary
20 amine derivative is a p-phenylenediamine
derivative.
4. Process according to any one of the claims 1-3,
characterized in that N-isopropyl-N'-phenyl-p-
phenylenediamine is used as antioxidant.
- 25 5. Process according to any one of the claims 1-4,
characterized in that the antioxidant is added
prior to hydrogenation.
6. Process according to any one of Claims 1-5,
characterized in that the hydrogenation is
30 carried out in the presence of a compound which
contains an element from group 13 of the periodic
system as catalyst, including the use as polymer
of NBR that is polymerized in the presence of a
polymerizable antidegradant.

7. Process according to any one of Claims 1-5, characterized in that the hydrogenation is carried out in the presence of a metal ion activator as catalyst.
- 5 8. Process according to any one of Claims 1-7, characterized in that the molar ratio of reducing compound/double bonds is between 0.9/1 and 2/1.
9. Process according to any one of Claims 1-8, characterized in that the molar ratio of
10 oxidizing compound/double bonds is between 0.9/1 and 2/1.
10. Process according to any one of Claims 1-9, characterized in that the oxidizing compound is added to the reaction mixture after hydrazine.
- 15 11. Process according to any one of Claims 1-10, characterized in that the polymer is present in the latex form.
12. Process according to any one of Claims 1-11, characterized in that the oxidizing compound is
20 hydrogen peroxide.

INTERNATIONAL SEARCH REPORT

Internat. Search No.
PCT/NL 00/00450

A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 C08C19/02

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C08C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

WPI Data, EPO-Internal

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 5 068 313 A (SCHIESSL HENRY W) 26 November 1991 (1991-11-26) abstract; claims; example 1	1,2,8-12
X	US 5 221 714 A (PARKER DANE K) 22 June 1993 (1993-06-22) cited in the application abstract; claims; example 1 column 4, line 5 - line 25	1,2,8-12
A	US 5 057 601 A (MIGLIARO JR FRANCIS W ET AL) 15 October 1991 (1991-10-15) abstract; claims; example 1	1
A	US 4 452 950 A (WIDEMAN LAWSON G) 5 June 1984 (1984-06-05) cited in the application abstract; claims; examples	1
-/-		

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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Date of the actual completion of the international search

5 October 2000

Date of mailing of the international search report

17/10/2000

Name and mailing address of the ISA

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Mettler, R-M

INTERNATIONAL SEARCH REPORT

Internat. Search No.
PCT/NL 00/00450

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
P, X	<p>WO 00 09568 A (AAGAARD OLAV MARCUS ;BELT JOHANNUS WILHELMUS (NL); SINGHA NIKHIL K) 24 February 2000 (2000-02-24) abstract; claims; examples VIII, IX page 11, line 23 - line 30 -----</p>	1-12

INTERNATIONAL SEARCH REPORT

ma patent family members

Internat ion No

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